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DEVELOPMENT OF A PROTOTYPE NITRATE DETECTOR

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16. ABSTRACT

A semi-continuous prototype detector for suspended atmospheric nitrate was developed, designed, fabricated and tested. The sensing range of the resulting instrument was from less than 1 $\mu g/m^3$ to over 100 $\mu g/m^3$ of suspended nitrate with an analysis time of less than one hour. A series of ambient sampling tests were performed with the prototype instruments run in parallel to three high volume samplers. The results of these tests show that the instrumental measurement compares well with the high volume sampler measurements. Temporal variations in suspended nitrate concentration were monitored showing the feasibility of measuring the dynamic behavior of nitrate in the atmosphere.

The protype detector uses a LEAP sampler to collect atmospheric particulate into aqueous solution where the soluble nitrate is dissolved. The resulting solution is analyzed by an ionselective electrode technique for nitrate. Operating and calibrating functions may be controlled automatically or manually.

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by

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SECTION I

CONCLUSIONS

The results of this program indicate that a practical system for automatically sampling and analyzing for suspended nitrate can be successfully implemented.

The prototype nitrate monitor demonstrated adequate sensitivity to meet the 1-100 $\mu g/m^3$ concentration range specifications. Field results obtained over a range of about 1.7 $\mu g/m^3$ to 35 $\mu g/m^3$ were consistent with high-volume measurements taken as reference. The collection efficiency of the LEAP sampler was about 80%, as expected on the basis of the manufacturer's design characteristics. The monitor results, including a back-up filter, averaged about 80% of the high-volume results. The difference is believed to be due to the loss of large-diameter, nitrate-containing particles in the monitor intake system.

The sensitivity of the monitor at the lowest concentrations observed indicates that the monitor should be able to follow concentrations of the order of 1 $\mu g/m^3$ with a time resolution of 1 hour or less. Continuous measurements at 15 $\mu g/m^3$ and above appear reasonable. Since nitrate formation and removal dynamics must be understood before we are able to develop optimal control programs, this instrument should become a valuable scientific tool for the investigation of the fate of nitrogen oxides.

Further field operations need to be carried out to gain a fuller understanding of the ultimate sensitivity and time resolutions of the instrument, and to characterize better its accuracy and precision.

The instrument concept used in developing the continuous nitrate monitor is very general. By introducing appropriate means of analysis, other species, both anionic and cationic, can be monitored in a device of similar characteristics.

SECTION II

RECOMMENDATIONS

1. The present prototype, preferably without the inlet-mounted cascade impactor, should be used to study the dynamic behavior of atmospheric nitrates.

2. The prototype could be improved by the following:
   a) increase reliability through mechanical improvements;
   b) simplify operation as part of mechanical improvements above;
   c) increase fine particle collection efficiency of the electrostatic precipitation section of the LEAP sampler or using a larger type of LEAP sampler;
   d) lower the detection threshold by decreasing the collection solution volume in the system, probably by taking advantage of electrode miniaturization.

3. Additional field experience should be obtained in order to better characterize the instrument performance, and to establish a detailed basis for improvements.

4. Analytic schema for other species should be studied to assess the feasibility of extending the concept. NH_4^+ and $SO_4^=$ ions, for which specific ion-electrode analyses are available, appear to be excellent choices for such extension.

SECTION III

INTRODUCTION

Nitrate in atmospheric particles probably represents the atmospheric end product of the nitrogen oxides produced in combustion processes. The original sources of nitrogen oxides and the intermediate chemical steps are dynamic processes which vary not only from day to day but also during the course of a single day, due to automative traffic flow, solar radiation, etc. A useful tool in studying this dynamic process is a real-time nitrate monitor. At present, almost all data on suspended nitrate concentration has been collected by the National Air Sampling Network (NASN). These data were produced by the colorimetric analysis of the warm water extract from 24-hour, high-volume filter samples. Hence, from this data the finest time resolution on the behavior of suspended nitrate is day-to-day variations.

The one-day average concentration levels of suspended nitrate range from much less than 1 $\mu g/m^3$ to well over 10 $\mu g/m^3$. Summary data from the NASN are presented in Table 1. The particulate-bearing nitrate is in the fine particle size range. Data of Lee and Patterson [1] indicate that the particle size is approximately 0.4 μm (mmd).

The approach taken in developing a nitrate monitor is as outlined below. Suspended atmospheric particulate is sampled by use of a commercially available air sampler (Environmental Research Corp., LEAP Model 3440). LEAP samplers are designed to concentrate by a large factor, on a continuous basis, the particles in a large volume of air into a small volume of solution. In this approach aqueous collection solution is used and the highly soluble nitrate is dissolved. Then, the nitrate concentration of the resulting solution is analyzed with a nitrate ion-selective electrode technique using commercially available electrodes (Orion Re-

TABLE I

SUMMARY OF DATA FROM NASN AND CONTRIBUTING
STATE AND LOCAL NETWORKS

(Values in $\mu g/m^3$)

Pollutant	Urban			Non-Urban		
	No. of Stations	Arith. Average	Max. Station Average	No. of Stations	Arith. Average	Max. Station Average
Suspended Particulates	217	102	254	30	38	79
Nitrates	132	2.9	13.5	29	1.3	2.5
Nitrogen Dioxide (gas)	47	141	333			

search). The nitrate concentration of the solution is then related back to the suspended atmospheric nitrate concentration through the operating parameters of the system such as, sample air flow, solution volume, and time.

The principle design task in the program was the design and fabrication of an interface system between the LEAP sampler and the nitrate ion-selective electrode. This system incorporates the functions of solution handling, timing, calibration and sampling mode. In the following task evaluation of the system was performed. The design specifications for the monitor require automatic measurements of atmospheric nitrate concentrations from 1 to 100 $\mu g/m^3$ with an analysis time of one hour or less. The monitor designed and fabricated in this program successfully meets these specifications.

SECTION IV

DISCUSSION OF PROGRAM

A. GENERAL

The development program was divided into three phases, viz.

Phase I - Design
Phase II - Fabrication
Phase III - Delivery and Demonstration

B. PHASE I - DEVELOPMENT AND DESIGN

The Phase I activities were directed toward gathering background performance data on the LEAP sampler and the nitrate ion-selective electrode. Also criteria for sampling and calibration modes were established. An initial total design of the prototype instrument was generated and presented for Project Officer approval in an informal interim report and oral presentation.

C. PHASE II - FABRICATION AND EVALUATION

Following Project Officer approval of the initial design, fabrication of the instrument was implemented. Following fabrication the instrument was operated to determine suitable operating parameters such as flow rates, solution concentrations operation mode times. Also, preliminary sampling of atmospheric air was performed.

In the course of this evaluation a problem was observed, namely air bubbles attached to the sensing surface of the nitrate ion-selective electrode. When this happened data were lost unless the electrode was removed from the sensing cell and the gas bubble removed by washing the sensing surface with a

jet from a wash bottle. The scope of work was increased to eliminate this problem and also to modify the instrument for 7-day operation including the placement of a coarse screen and cascade impactor (~7 μm, cutoff) at the air sample inlet.

Additionally, a series of 10 comparative tests of the nitrate monitor with the high-volume samplers were included and performed in the increased scope of work.

D. PHASE III - DELIVERY AND DEMONSTRATION

After completing the Phase II Fabrication and Evaluation, the nitrate monitor was delivered to the EPA and operation of the prototype was demonstrated.

SECTION V

INSTRUMENT

A. GENERAL

1. SAMPLING AND ANALYSIS CONCEPTS

The concept behind the design of this monitor is the concentration of the particles from a large volume sample of ambient air into a very small volume of solution. The very soluble nitrate compounds in the particles are readily dissolved. The resulting solution is then analyzed by a nitrate ion-selective electrode. Figure 1 depicts a block diagram of this process. The LEAP sampler performs the functions of air sampling and concentrating the sampled aerosol into a collecting solution. The interface provides control for two sampling modes and two electrode calibration modes. The electrodes used are a nitrate ion-selective and a fluoride reference electrode. The millivoltmeter measures and displays the electrical potential difference between the nitrate and reference electrodes.

The general relationship between the measured nitrate concentration in solution and the suspended nitrate in the atmosphere is given by the following general relationship:

$$C = c\frac{v_\ell}{v_a} \qquad (1)$$

where

C is the atmospheric nitrate concentration

c is the solution nitrate concentration

v_ℓ is the solution volume

v_a is the sampled atmospheric volume

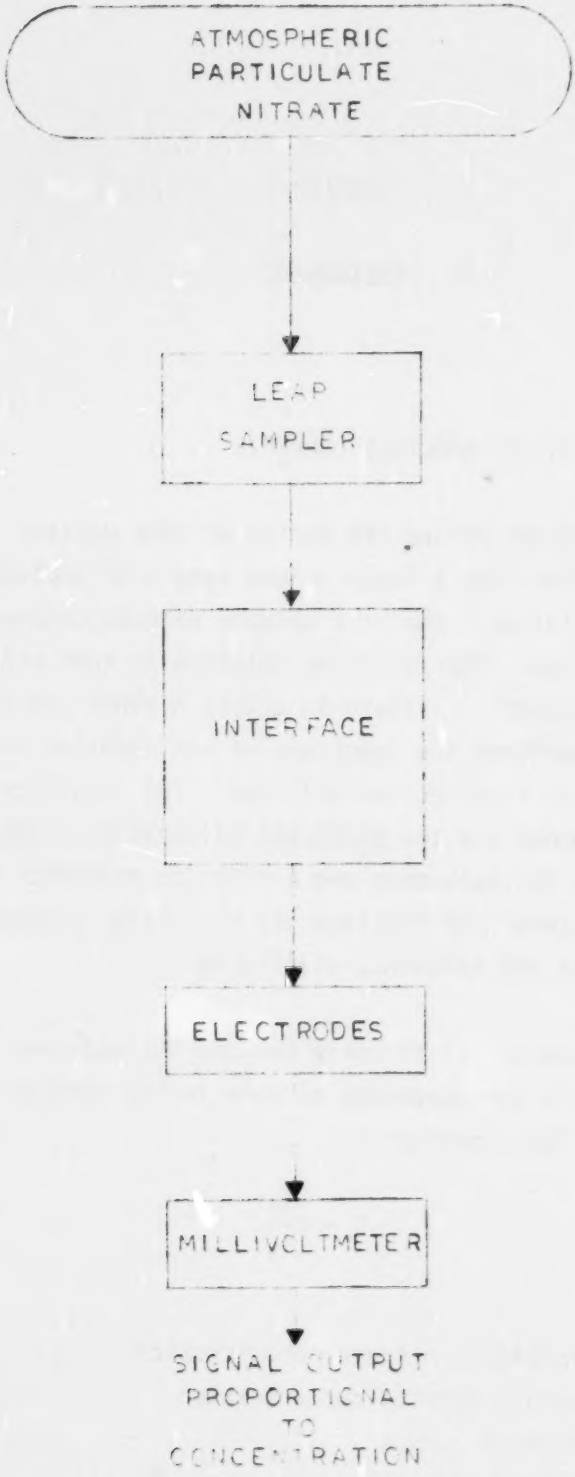


Figure 1. Nitrate Detector System.

This monitor has two sampling modes, continuous and recirculation. In the continuous mode, solution is passed only once through the system, and in the recirculation mode, solution is recirculated for a fixed time period.

For the continuous mode of operation, Equation (1) is rewritten in terms of the flow rates, viz.,

$$C = c\frac{q}{Q} \qquad (2)$$

where

Q is the air sample rate

q is the solution flow rate

If the threshold of the nitrate ion-selective electrode is taken at ~5 x 10^{-5} molar and if the air sample rate and solution flow is taken at ~600 ℓ/min and ~3 ml/min respectively, then the threshold sensitivity of the detector is ~15 μg/m^3.

For the recirculation mode of operation, Equation (1) is rewritten in terms of air sample rate and sample time (t), viz.,

$$C = c\frac{V_\ell}{Qt}$$

If the operating parameters from the above calculation are used with 60 ml of recirculation solution and a sample time of 60 min, then the threshold sensitivity is ~1 μg/m^3. Note however any threshold sensitivity may be achieved by a longer sampling time.

For both modes, the higher limit of detection is four decades higher than threshold, due to the four decade range of the nitrate electrode.

The electrode measurement is the potential difference between the nitrate and fluoride ion-selective electrodes. At operating conditions the potential of the nitrate ion-selective electrode is given by:

$$E_1 = E_{o1} - \frac{2.3\eta RT}{F} \log [NO_3^-]$$

and at the fluoride electrode by,

$$E_2 = E_{o2} - \frac{2.3\eta RT}{F} \log [F^-]$$

where

E_o = reference potentials

$\frac{2.3\eta RT}{F}$ = Nernst constant (~59 mv/decade)

$[NO_3^-]$ = nitrate concentration

$[F^-]$ = fluoride concentration

The millivolt meter reading (E) is the difference between these two potentials, viz.,

$$\Delta E = E_1 - E_2 = \Delta E_o - \frac{2.3\eta RT}{F} \log [NO_3^-] - \log [F^-]$$

or

$$\Delta E = \Delta E_o - \frac{2.3\eta RT}{F} \log \frac{[NO_3^-]}{[F^-]}$$

Rearranging the last equation we see that the nitrate and fluoride concentration ratio is actually measured, i.e.,

$$\frac{[NO_3^-]}{[F^-]} = \exp\left[-\frac{(\Delta E - \Delta E_o)\,F}{2.3nRT}\right]$$

This relation also holds for the ratio of the mass of nitrate ion and fluoride ion in the system. The collecting medium used in the monitor contains fluoride ion of known concentration, sufficiently large that the small amounts of fluoride ion or cations that tie up fluoride ion present in the atmosphere will not significantly change the concentration. The solution used in these experiments contained 10^{-4} molar fluoride ion concentration.

Changes in the collection medium volume due to evaporation or dilution from atmospheric condensation over the collecting plate will not affect the analytic results.

2. DESCRIPTION OF THE PROTOTYPE INSTRUMENT

In final form, the prototype nitrate detector has plumbing, valving and timing devices to permit sampling in either the continuous mode, or more importantly in terms of sensitivity, in the recirculate mode. Provisions exist for calibrating the ion-selective electrode by injection of two levels of calibration solution either automatically or manually. Provision is made for stablizing the temperature of the test solution by a temperature sensor controlling arc immersion cooler in the cell and for eliminating nonhomogenetics by stirring the solution in the cell. The liquid level sensor/controller is provided to prevent the system from drying out due to evaporation while operating in the recirculate mode. A schematic of the monitor showing the various sub-systems is shown in Figure 2. A pictorial layout is shown in Figure 3. A descriptive list of specific components is presented in Appendix A.

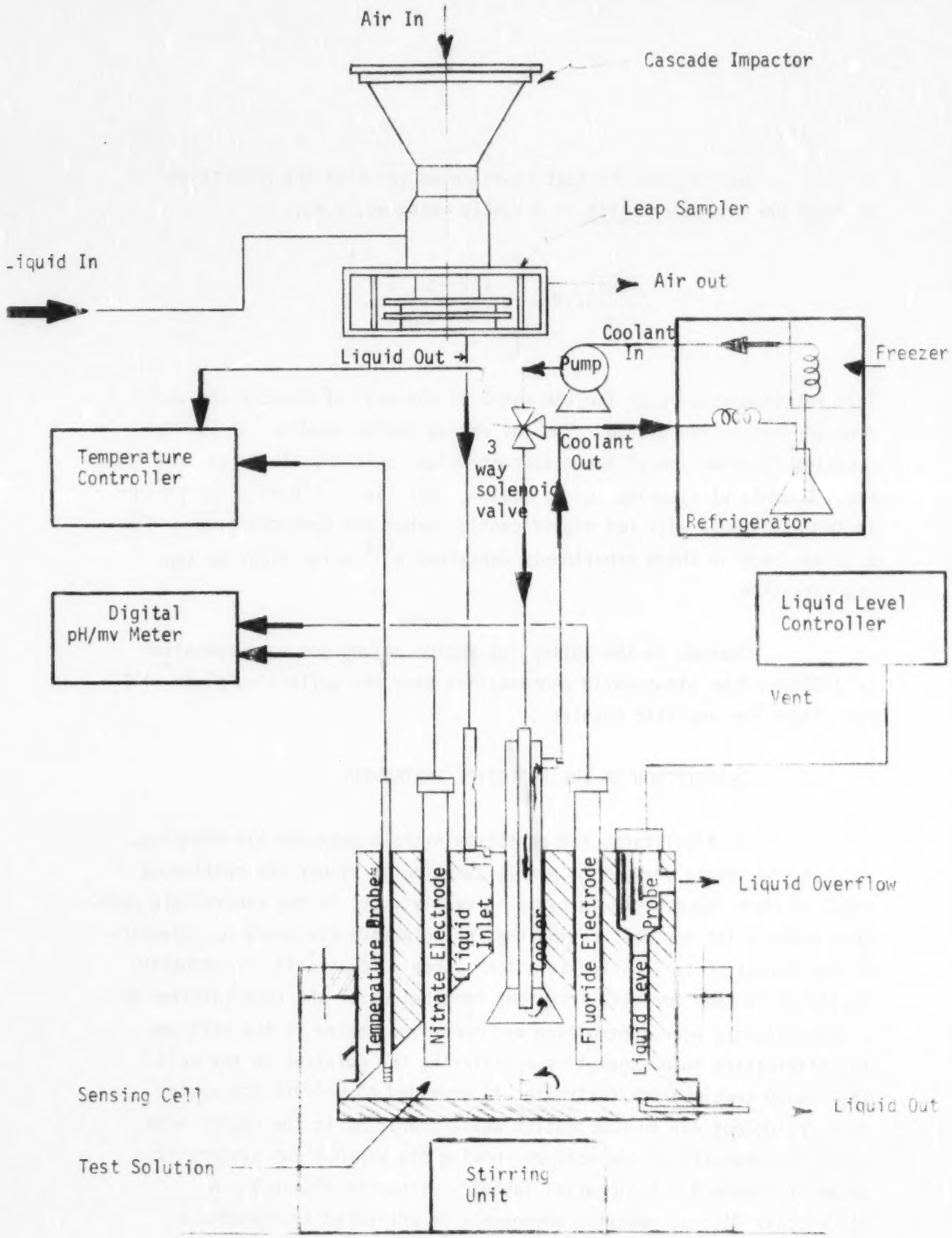


Figure 2 Schematic of Nitrate Monitor With Cascade Impactor

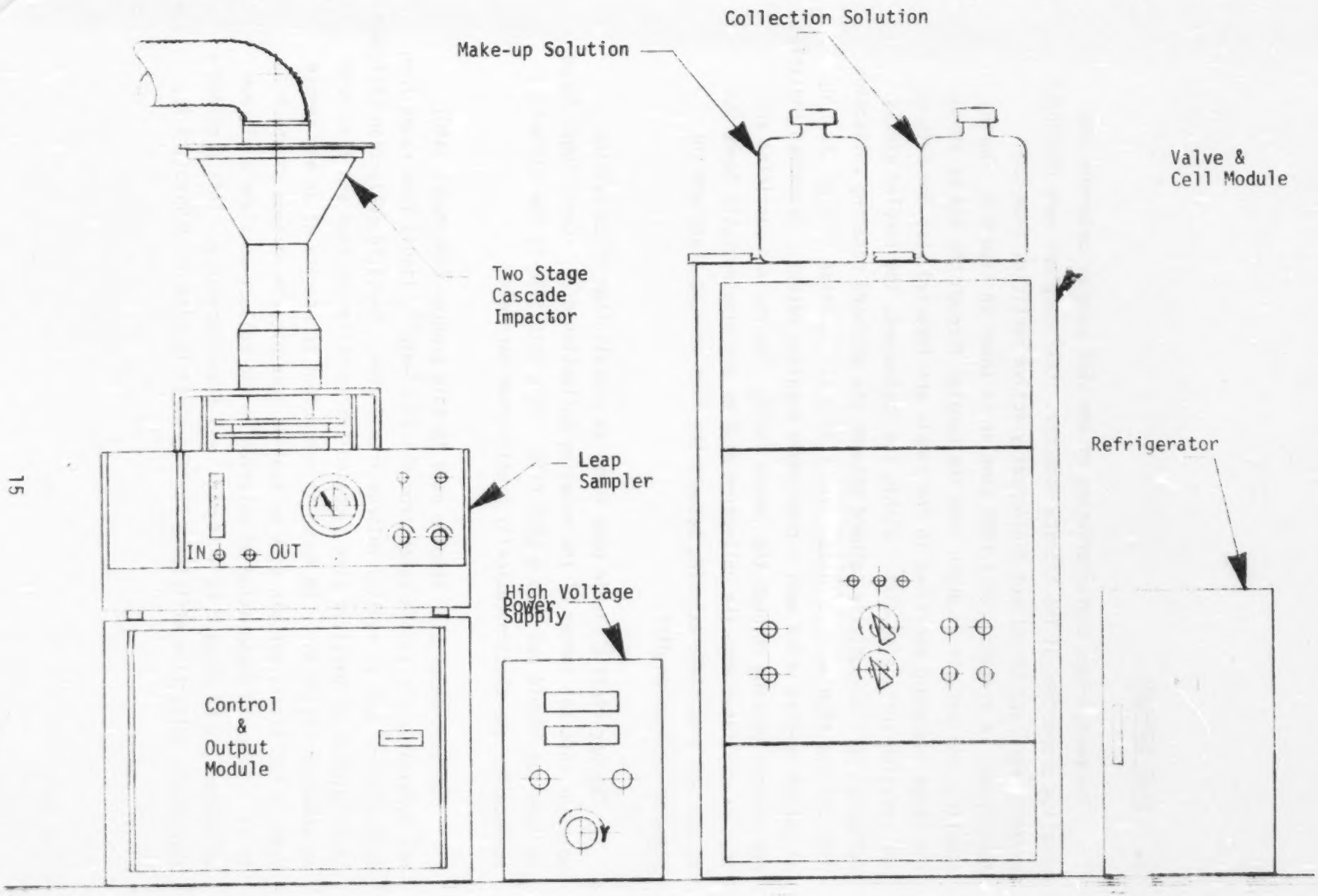


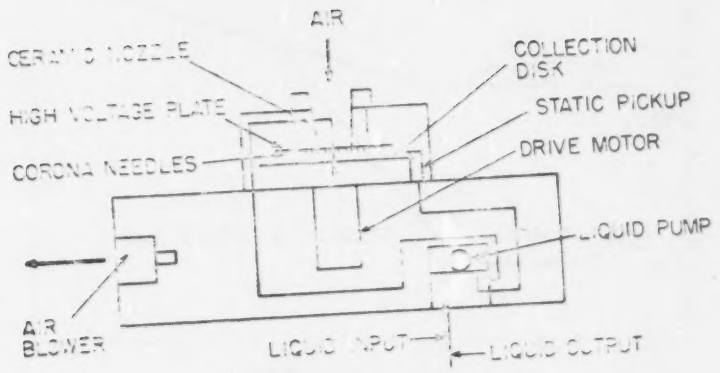
Figure 3. Physical Layout

B. LEAP SAMPLER

The performance characteristics of the LEAP sampler determine the sampling properties of the Nitrate Detector. LEAP samplers were developed several years ago to collect biologically active particles from the atmosphere. A schematic of a LEAP sampler is shown in Figure 4. During sampling, ambient air is drawn into the sampler through the top as shown. The large suspended particles in the sample are impacted near the axis of the rotating collection disk. Within the instrument, the sampled air is deflected to flow radially outward between the grounded rotating collection disk and the high voltage plate. The sample air is drawn through the ring of corona needles which emit a continuous negative corona. Suspended particles are charged passing through the corona field. The charged particles are then precipitated onto the collection disk by the electrostatic force due to the electric field existing between the high voltage plate and the grounded collection disk.

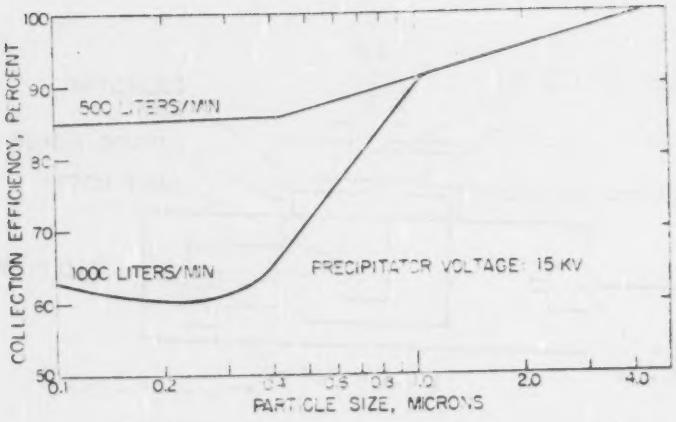
The peristaltic liquid pump supplies a small flow of collection solution onto the center of the rotating collection disk. Centrifugal force spreads the liquid out into a thin film. This thin film is the collection surface for the electrostatically precipitated particles.

The particular LEAP sampler used in this program (ERC Model 3440) has adjustable air sample rates from 0-1.20 m^3-min^{-1}, liquid flow rates from 0-10 ml-min^{-1} and an applied voltage from 0-20kv. Particle collection efficiency is a function of particle size, applied precipitation voltage and flow rate as shown in Figure 5. We found it convenient to operate at an air sample rate of 600 liters per min with an applied precipitator voltage of about 15 kv. To avoid evaporation of solution on the collection plate a minimum solution flow of about 3 to 4 ml-min^{-1} was found necessary. This provided a reasonable collection efficiency for the particle size of interest, i.e.,



Schematic of EMP sampler (after ERC Catalog 1969-1970).

Figure 4



LEAP collection efficiency (after ERC Catalog 1969-1970).

Figure 5

~0.4 μm. Further discussion on collective efficiency is presented in the section on results.

The LEAP sampler is a very poor collector of gases. This is shown by calculation in Appendix B. For this reason, the Nitrate Detector is not expected to be affected by such gaseous interferences as NO_2.

C. ION-SELECTIVE ELECTRODES

As stated earlier in the general description of the instrument, a nitrate ion-selective electrode is used to sense the nitrate ion concentration of the resulting collection solution and a fluoride ion-selective electrode is used as a reference electrode. The nitrate and fluoride ion-selective electrodes are Orion Research Models 92-07 and 94-09 respectively. The ion-selective electrode sensing was selected for simplicity and ease of application over the more procedurally complicated colorimetric procedures of nitrate analysis.

A manual method using these electrodes has been investigated for measuring suspended nitrate concentration. The results of this study are discussed by Williams, et al., 1972. In the course of this study it was shown that the possible interferences due to Cl^-, Br^-, I^-, VO_3^- and SeO_4^- may be eliminated by precipitation out of the measurement solution by adding silver fluoride. As indicated by Driscoll and Forney, 1973, and Williams, et al., 1972, Br^- from automobile exhaust is the most likely interference. As a precaution the collection solution has been doped with a concentration of 10^{-4} molar AgF. Since the nitrate ion-selective electrode selectivity constant $K_x = 0.13$ for Br^- versus $K_x = 1$ for nitrate, and $AgBr^-$ is virtually insoluble; the Br^- interference is removed from at least equal concentration of Br^- and NO_3^-.

D. INTERFACE SYSTEM

1. GENERAL FUNCTIONS

The functions of the interface system is the following:

a. convey liquid sample from the LEAP sampler to the electrodes

b. control the sample modes

c. control the calibration modes
d. program the flush cycle on recirculation sampling
e. thermally stabilize the electrode measurement
f. control volume of recirculation solution
g. mix the sample solution

A schematic of the elements of interface system is shown in Figure 2. Figure 6 shows a solenoid valve interconnecting diagram of the system connecting the LEAP sampler with the electrode in the cells. When the Detector is operating in the continuous sampling mode solution is pumped out from the LEAP sampler through V4 to the cell. Solution from the cell pumped through V2 to the LEAP sampler. Any decrease in recirculation solution volume due to evaporation is sensed and deionized water is added through V9 to maintain constant solution volume. At the end of a sample cycle the recirculation solution is flushed out and replaced by fresh collective solution. The flush is initiated either automatically or manually. Collection solution flows under gravity through V8 to the cell. Solution from the cell flows out through the overflow indicated. Fresh solution is also pumped into the LEAP sampler through V1. (It is necessary to maintain a continuous flow on the collection plate of the LEAP sampler or liquid will be splashed about shorting out the applied high voltage).

During calibration, calibration solution flows through either V5 or V6 to the cell. Solution in the cell flows out the indicated overflow port.

The valve position for each function is shown in Table 2. The method of controlling the solenoid valves is shown in Figure 7. Figure 8 shows the wiring schematic for the solenoid valve switching and timing.

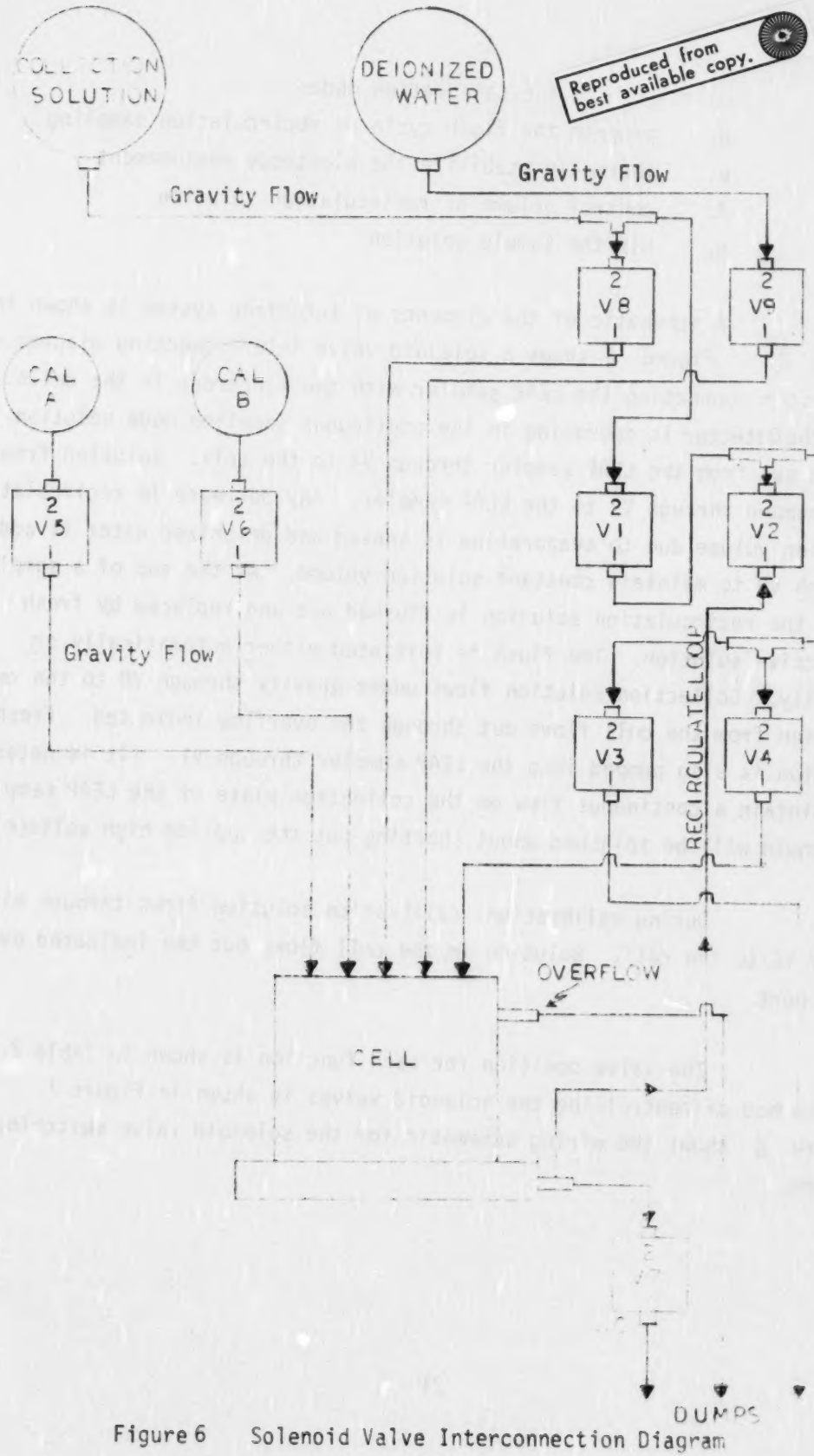


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Figure 6 Solenoid Valve Interconnection Diagram

TABLE 2

VALVE POSITION

Continuous

	V_1	V_2	V_3	V_4	V_5	V_6	V_7	V_8	V_9
Open	X			X					
Closed		X	X		X	X	X	X	X

Calibration A

	V_1	V_2	V_3	V_4	V_5	V_6	V_7	V_8	V_9
Open	X		X		X				
Closed		X		X		X	X	X	X

Calibration B

	V_1	V_2	V_3	V_4	V_5	V_6	V_7	V_8	V_9
Open	X		X			X			
Closed		X		X	X		X	X	X

Recirculate

	V_1	V_2	V_3	V_4	V_5	V_6	V_7	V_8	V_9
Open		X		X					(On Demand)
Closed	X		X		X	X	X	X	

Flush Between Recirculation

	V_1	V_2	V_3	V_4	V_5	V_6	V_7	V_8	V_9
Open		X		X				X	
Closed	X				X	X	X		X

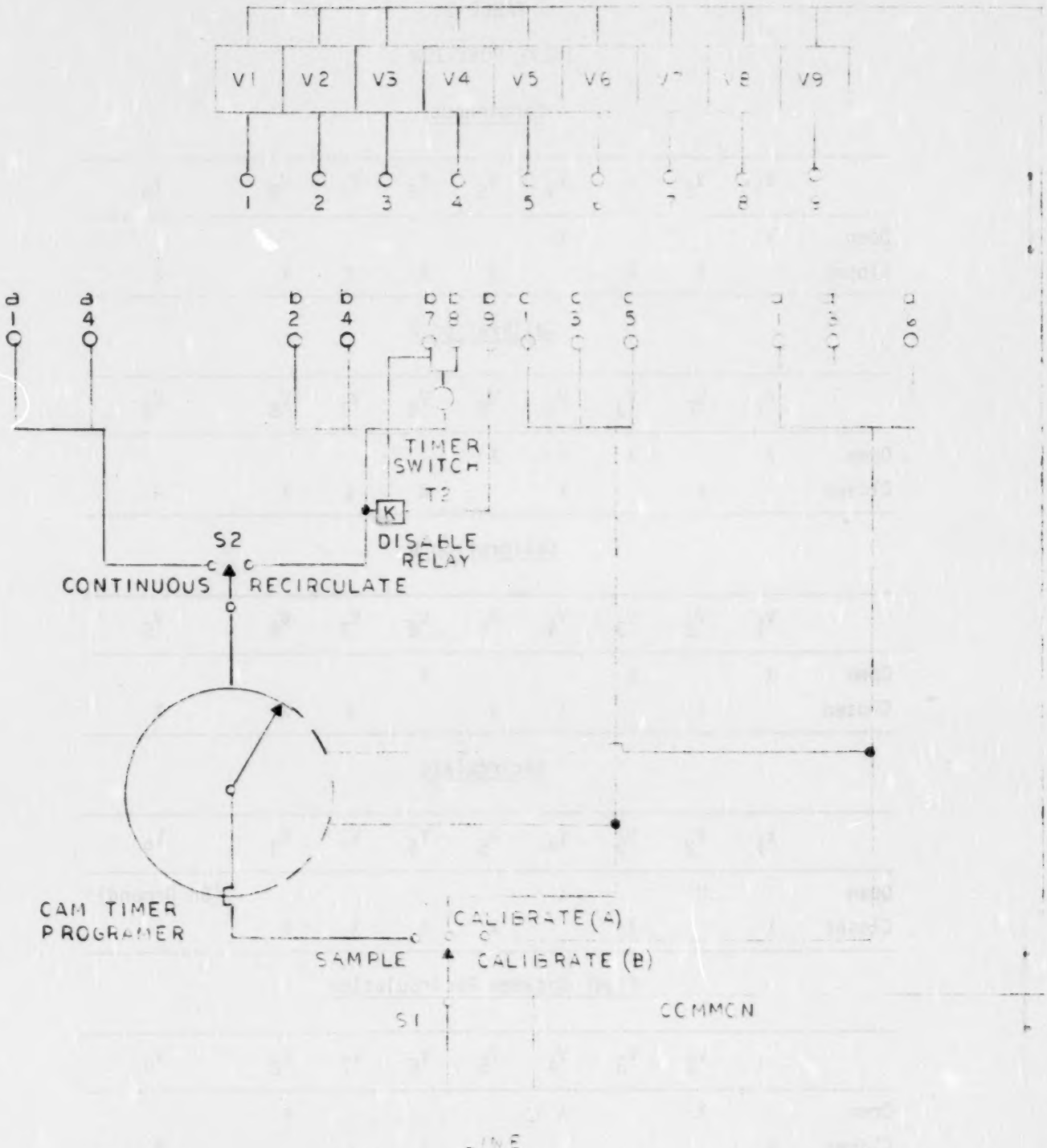
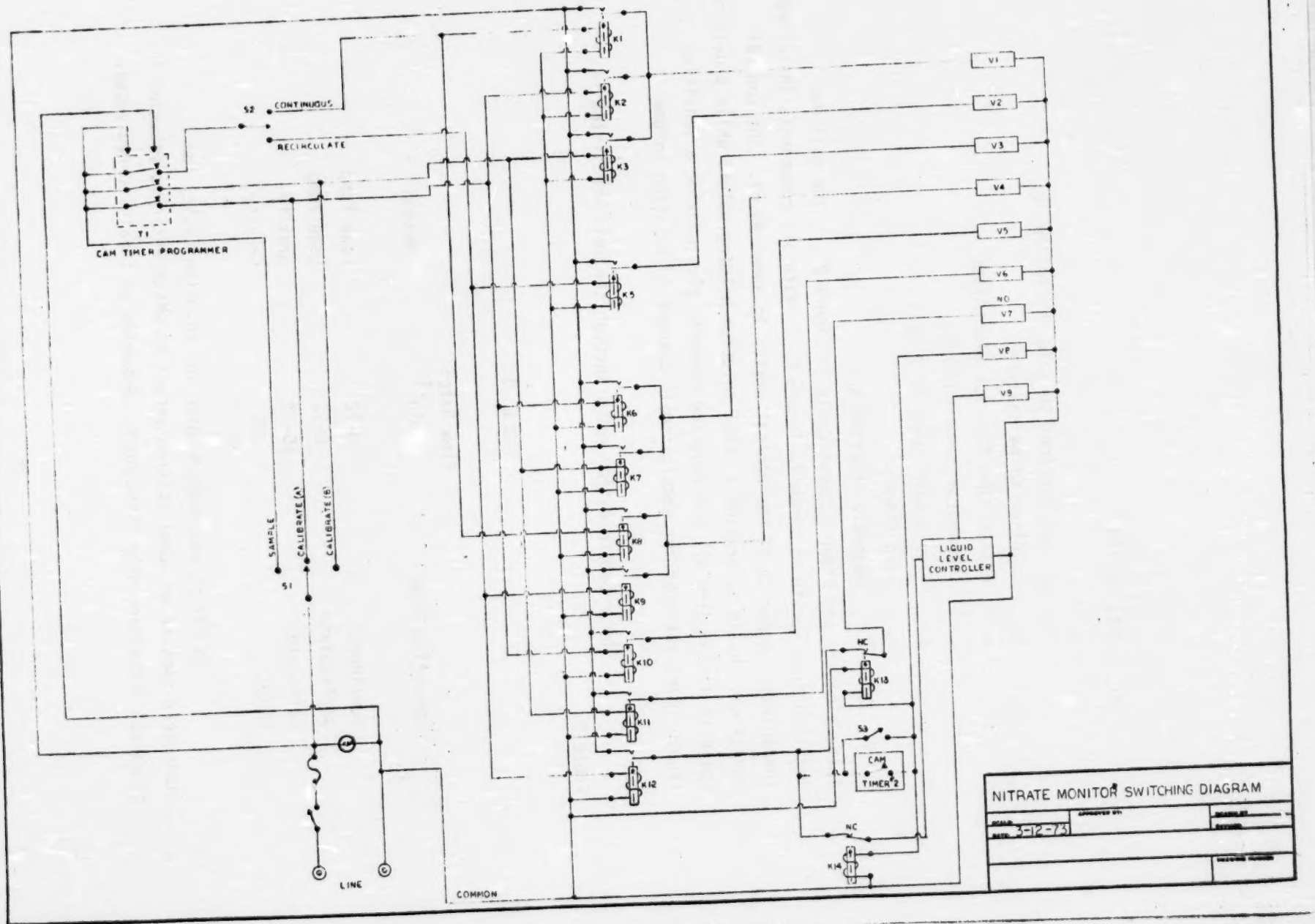


Figure 7 Program Valve Diagram

Figure 8 Switching Circuits Design



2. CELL DESIGN

The cell was designed to hold the following:

a. solution to be analyzed
b. nitrate and fluoride electrodes
c. temperature sensing probe
d. liquid level sensing probes
e. cold finger
f. magnetic stirring bar

These elements are shown schematically in Figure 2. The cell was machined from lucite as shown in Figure 9. With all components installed the solution capacity of the conical cavity is about 45 ml. The conical cavity was chosen to provide a small solution holding volume while providing space to accommodate all the required elements plus provide a sensitive liquid level detector for sensing small changes in solution volume.

The volumetric flow rates through the cell are listed in Table 3.

TABLE 3

Operating Mode	Flow Rates ml min^{-1}	Method
Continuous	0-12	Leap Pump
Recirculate	0-12	Leap Pump
Calibrate	15-20	Gravity
Flush	~25	Gravity

An effort was made to give the solution cavity the characteristics of an ideal stirred vessel in which entering solution is dispersed instantaneously throughout. Assuming an ideal stirred vessel

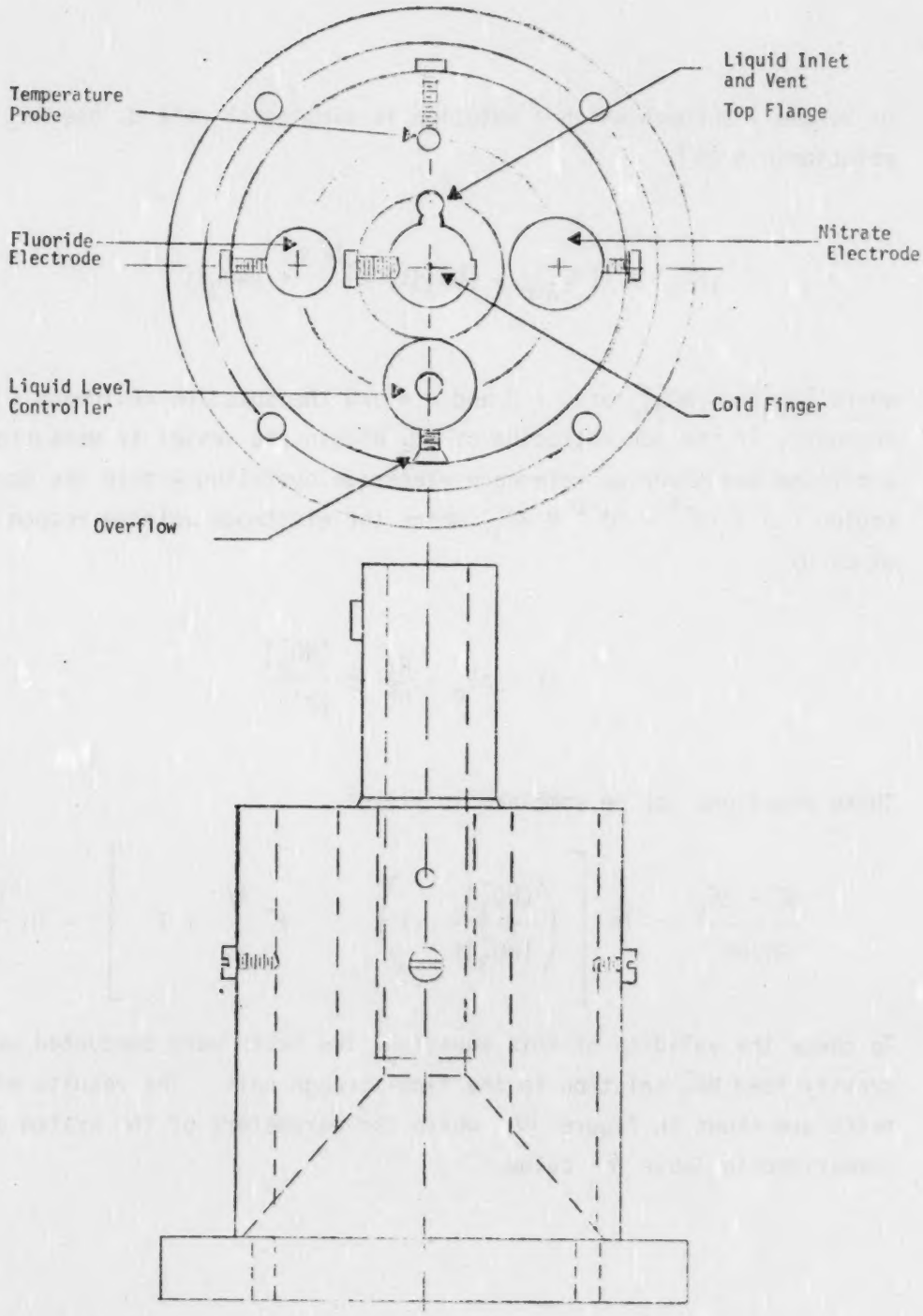
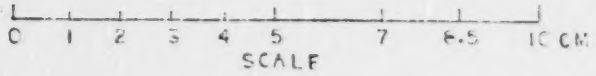


Figure 9 Cell Arrangement



of volume V through which a solution is slowing at rate Q, one has the relationship [4].

$$[NO_3^-] = ([NO_3^-]_o - [NO_3^-]i)\, e^{-t/\tau} + [NO_3^-]i$$

where $[NO_3^-] = [NO_3^-]_o$ at t = 0 and τ = V/Q the solution residence time. Moreover, if the concentration of NO_3^- within the vessel is measured with a nitrate and fluoride reference electrode operating within the Nerstian region (~5 x 10^{-5} - 10^{-2} M NO_3^-) where the electrode voltage response is given by

$$\Delta E = \Delta E_o - \frac{RT}{nF} \ln \frac{[NO_3^-]}{[F^-]}$$

These equations can be combined to yield:

$$\frac{\Delta E - \Delta E_o}{RT/nF} = -\ln \left[\left(\frac{[NO_3^-]_o}{[NO_3^-]i} - 1 \right) e^{-t/\tau} + 1 \right] - \ln \frac{[NO_3^-]i}{[F^-]}$$

To check the validity of this equation, two tests were conducted using a gravity feed NO_3^- solution to the flow-through unit. The results of both tests are shown in Figure 10, where the parameters of the system are summarized in Table 4 below.

TABLE 4

UNIT TEST PARAMETERS

ΔE_o = 73 mv

RT/nF = 26.9

T = 38.5°C

n = 1

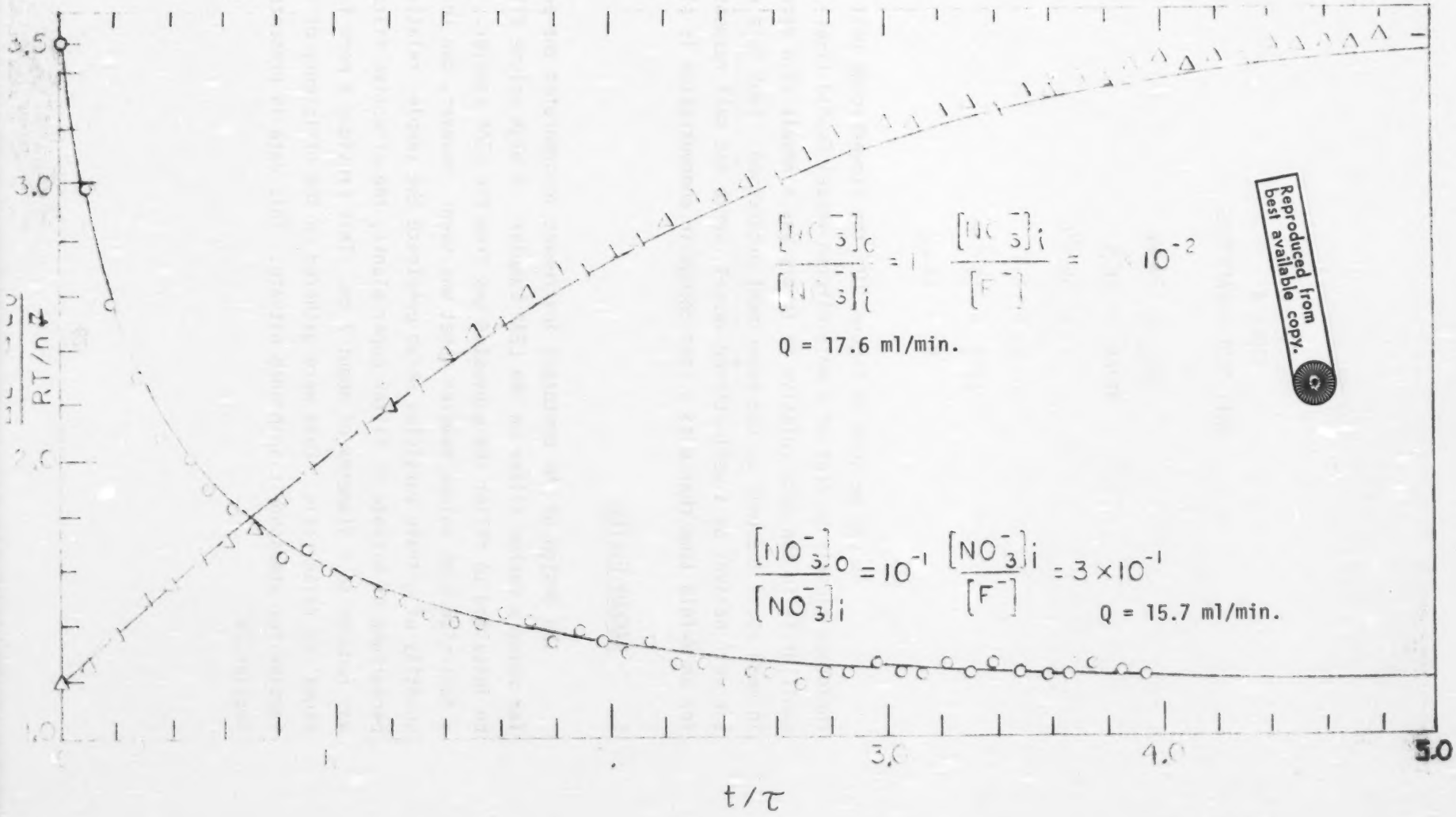
$[F^-]$ = 10^{-2} M

V = 44 cc.

As can be seen in Figure 10 the flow-through unit response conformed closely to that of a well-stirred vessel (solid lines). The small drift in the data relative to theory was a result of a decrease in head above the unit as the experiment progressed. From this result the cell behaves as a well-stirred vessel, hence the cell response time for an e-fold time chance to a step change in concentration is simply V/Q.

E. BACKUP FILTER

The design of the prototype instrument incorporated the provision for using a backup filter on the LEAP sampler. A high volume filter may be installed to filter the exhausted gas from the LEAP sampler. Originally a full-size high volume sampler sheet was used. However, due to the small quantity of nitrate particles which penetrate the sampler relative to the background of nitrate or filter paper blanks, the effective filtering area was reduced to a diameter of about 7 cm. This provided a more favorable signal to raise ratio. Data were gathered on the efficiency of the LEAP sampler for atmospheric suspended nitrate. This data is presented in the Section IV.



Reproduced from best available copy.

Figure 10 Cell Response

F. INLET IMPACTOR

A contract requirement was the installation of our impactor with a particle cut-off of 7 ± 2 μm. Upstream of the LEAP sampler inlet, a BGI-30 (BGI-Incorporated) high volume cascade impactor was installed to remove the particles greater than approximately 7 ± 2 μm. The BGI-30 is a four stage impactor (Figure 11) with particle penetration characteristics as shown in Figure 12 for a sample flow rate of 0.85 m^3-min^{-1}. Since the LEAP sampler is operated at 0.60 m^3-min^{-1}, the particle size penetration was assumed to be approximated by increasing particle size by the ratio of the flow rates. For example the 50% penetration of the second stage (Figure 12) is taken as:

$$\text{Particle size} = 3.8\ \mu m_x \frac{.85\ (m^3\text{-}min^{-1}}{.60\ (m^3\text{-}min^{-1}} = 5.4\ \mu m$$

Since this is within our tolerance of 7 ± 2 μm, the impactor was used with the first two stages installed. Actual penetration was not measured.

In conventional impactor operation, the collection stages are greased to decrease re-intrainment of impacted particles. However, in our operation where it was required to measure the total nitrate in the sample stream, the stages were not greased because the grease interferred with a subsequent manual analysis (ion-selective electrode method) for nitrate on the collection stages.

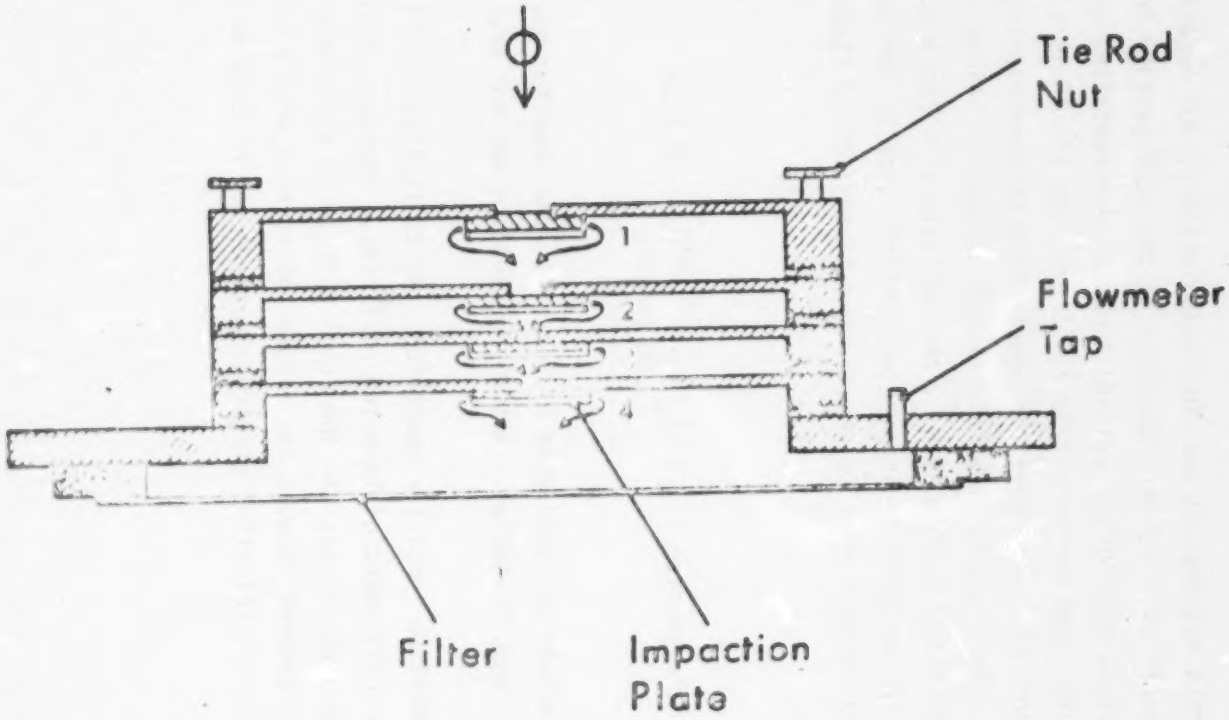


Figure 11 Schematic Cutaway View of Impactor

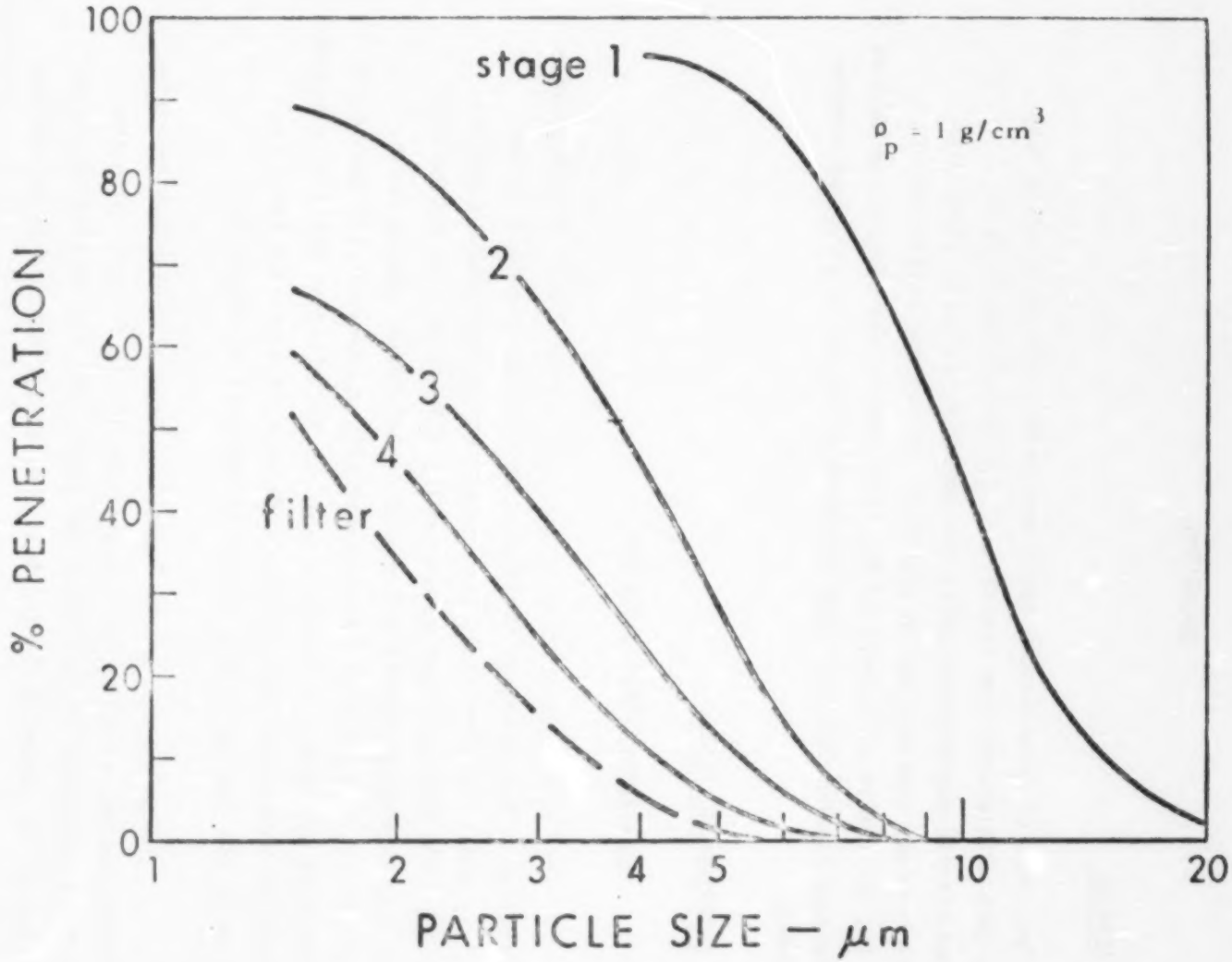


Figure 12 Stage Calibration Curves

SECTION VI

OPERATION

A. GENERAL

Two types of experimental tests were made. The first was a test of long-term maintenance-free operation. The second was a set of suspended nitrate measurements using the prototype detector along with three high-volume samplers run in parallel. During the latter set of tests, the collection efficiency of the LEAP sampler was measured as well as the difference between the prototype measurement and the high-volume sampler measurement.

B. EXPERIMENTAL TESTS

1. MAINTENANCE-FREE OPERATION

One objective of this test was to obtain 7 days of maintenance-free operation. The prototype instrument was set-up to sample in the recirculate mode. In this mode, the instrument recirculated collection solution for 105 minutes, then automatically flushed out the system (15 minutes) and initiated another 105 minute recirculation sample cycle. Every six hours, the analyzer was automatically calibrated with two levels of calibration solution. A liquid filter was installed at the liquid output from the LEAP sampler to trap the preponderance of insoluble particles collected by the sampler. This filter is depicted in Figure 13.

The test ended after almost four days of continuous operation. Termination was due to particles clogging the liquid filter. Also the liquid level controller failed about the same time, due to fine particles collecting on the grounded electrode of the sensor probe, thus insulating

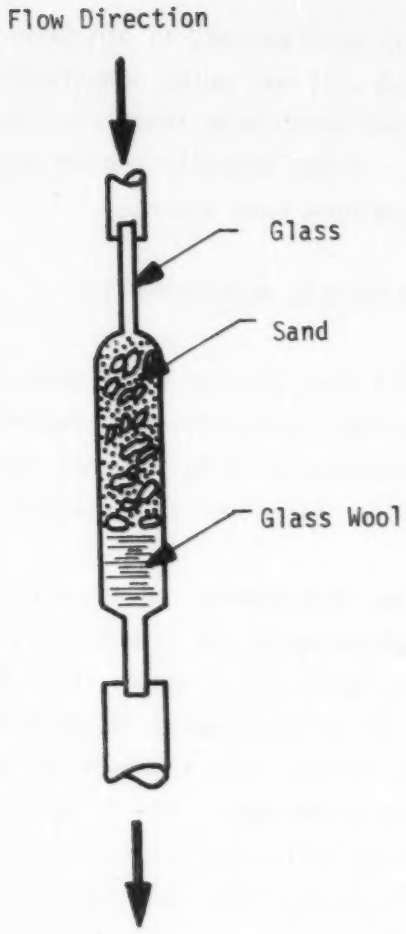


Figure 13 Filter

this electrode from the level sensing system. It was also observed that the tubing of the peristaltic pump in the LEAP sampler had begun to leak. (This tubing had considerably more than four days of testing and this failure was not a direct result of this test.)

During this test period, an old five-story building across the street from the test-site was being demolished. This produced very heavy dust concentrations which made these four days an extremely severe test of the instrument. Under ordinary conditions, a much longer uninterrupted test period could have been expected.

2. SUSPENDED NITRATE MEASUREMENTS

A series of ten, 24-hour tests were run in which the ambient atmosphere at our Cambridge facilities was sampled for suspended nitrate concentration. The prototype Nitrate Detector was operated with inlet impactor and backup filter installed as explained in Section V.

The referee measurement consisted of three high-volume sampler measurements made simultaneously and in proximity to the sample intake of the prototype detector, which was a conventional hi-vol shelter. There were about 6-8 meters of 10 cm diameter flexible hose connecting the detector to the sample intake. All analyses for nitrate were performed by selective ion electrode techniques. All filter and impaction stages were extracted and analyzed by techniques similar to those reported by Williams et al.[2] Nitrate collected by the LEAP sampler was analyzed automatically in the detector cell.

The results are presented in Table 5. Detailed data for individual tests are presented in Appendix C. In reporting the results, the impactor catch is summed with cell collection and reported as the "Detector Results." These values are summed because the impactor is not a

TABLE 5

RESULTS

Test No	Hi-Vol Results ($\mu g/m^3$)	Mean	Std. Dev.	Detector Results ($\mu g/m^3$)	Total Catch ($\mu g/m^3$)	Impactor Catch ($\mu g/m^3$)	Backup Filter Catch ($\mu g/m^3$)	Sample Cycle Time
1	13.3 12.5 14.0	13.3	.7	7.1	8.3	0.6	1.2	24 hr.
2	5.1 4.9 4.9	5.0	.1	4.3	4.7	0.4	0.4	24 hr.
3	4.7 4.3 4.7	4.6	.2	3.7	4.4	0.4	0.7	24 hr.
4	4.4 4.5 5.2	4.7	.4	3.1	3.8	0.1	0.7	1.75 hr.
5	1.7 1.4 2.0	1.7	.3	2.1	2.7	nil	0.6	1.75 hr.
6	3.0 2.7 4.0	3.2	.7	1.5	2.0	0.1	0.5	1.75 hr.
7	7.1 6.7 7.6	7.1	.4	1.9	2.5	0.2	0.6	1.75 hr.
8	35.5 24.6 45.7	35.5	10.5	4.1	4.9	0.6	0.8	1.75 hr.
9	9.9 3.9 4.7	4.5	.5	3.7	4.6	0.4	0.9	24 hr.
10	1.7 1.7 2.1	1.8	.2	1.8	1.8	nil	not used	24 hr

necessary element for the operation of the Nitrate Detector, and it is assumed that the large particles caught in the impactor would be readily caught by the LEAP sampler, then analyzed automatically by the cell if the impactor was not installed. The sum of the "Detector Catch" and the backup filter catch is reported as "Total Catch".

For five of the ten days of testing the detector was operated continuously in recirculation mode for 24 hours. In the remaining five tests the detector was operated in two-hour cycles with recirculation sampling for 1.75 hours and flush for 0.25 hours. The average of values for the 2 hour cycle is reported as the 24-hour value. The operation mode for each test is indicated in Table 5 under "sample cycle time."

The results from these tests indicated that the Nitrate Detector performs well. The "total catch" on the average was about 80% of the high-volume sampler measurement, with moderate scattering. The failure to account for all nitrate is thought to be due, in part at least, to the loss of nitrate present on large particles in the sampling line connecting the Detector to the sample inlet. Variations in the quantity of nitrate on large particles and/or variations in the large particle size distribution could result in the variability of the "total catch" results relative to the hi-vol determination. The "detector results" are about 81% of the "total catch". This result is as expected due to the collection efficiency of the LEAP sampler and previously reported particle size (mmd) for nitrate bearing particles in the atmosphere [1].

3. TEMPORAL VARIATION OF SUSPENDED NITRATE

During the test period temporal variations of suspended nitrate were measured. These data were collected in tests where the Nitrate Detector was operated with a 1.75 hour sample recycle time

(see Figure 14). These data are important, since it is the first data we know of which shows the temporal variation of suspended nitrate within a 24-hour period, and it indicates that this prototype instrument is capable of obtaining the dynamic data needed for experimentally investigating models for the fate of oxides of nitrogen in the atmosphere. Since only the cell collection fraction of the suspended nitrate is shown (the impactor collected the large particle fraction, ~7 μm) care should be used in theorizing with the data presented.

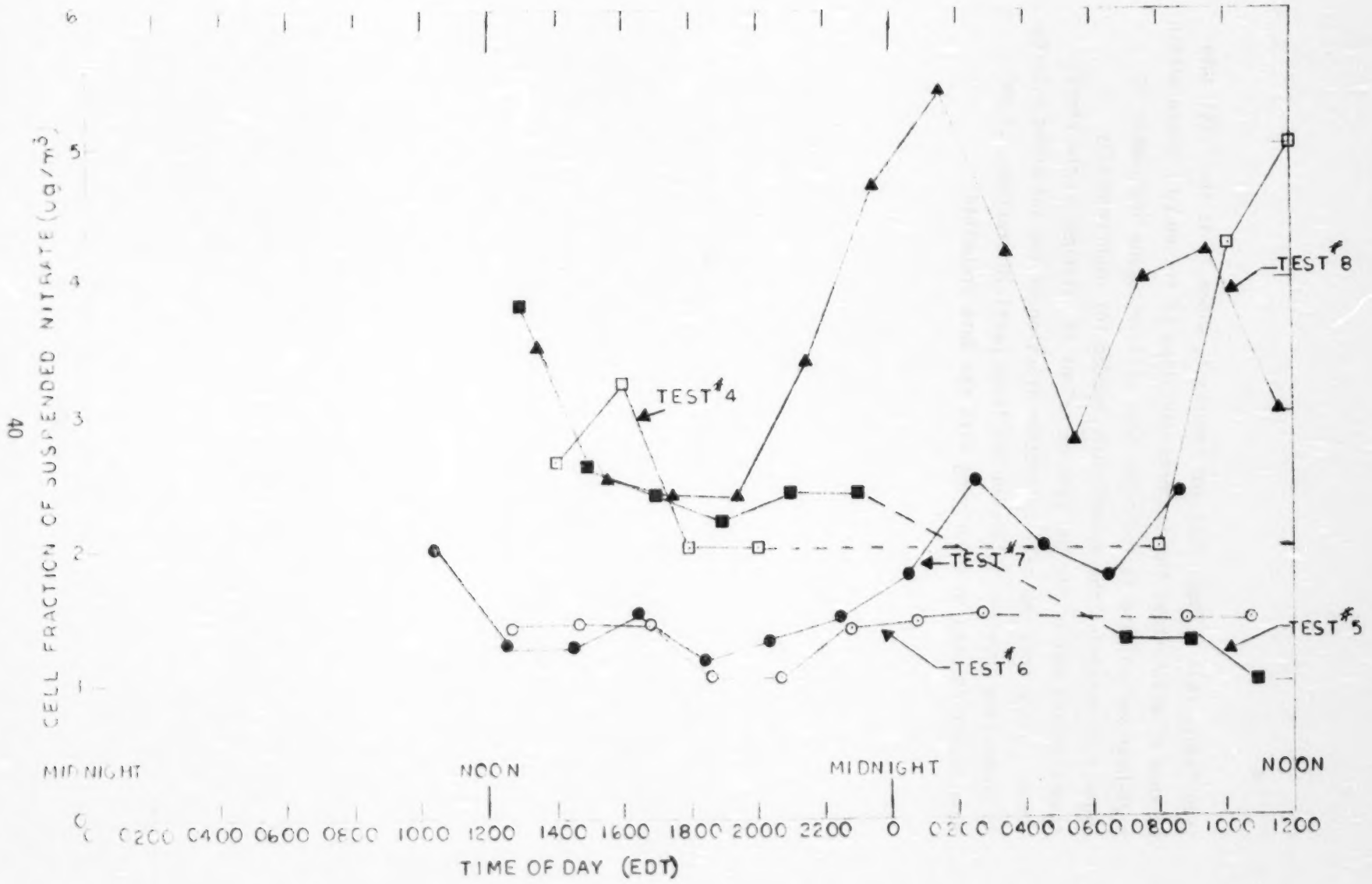


Figure 14 Temporal Variations

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2. William, D., J. Driscoll, C. Curtin and R. Hebert, "Methods for the Rapid and Accurate Measurement of Nitrate and Sulfate in Atmospheric Particles", Final EPA report on Contract No. 68-02-0564, EPA-650/2-73-050, December,1973.

3. Driscoll, J. and L. Forney, Chapter 8, Analytical Methods Applied to Air Pollution Measurements, Stevens and Herget (eds.), Ann Arbor Science Publisher, Ann Arbor, 1974.

4. Perry, J.H. (Ed.), Chemical Engineers' Handbook McGraw-Hill (1963)

APPENDIX A
LIST OF COMPONENTS

Component	Description
Electrode, Nitrate	Orion Model 92-07
Electrode, Reference, Fluoride	Orion Model 94-09
Electrode Meter (pH/mv)	Orion Model 701
Cell and base	Fabricated from Plexiglass
Lead Sampler	Environmental Research Corp. Model 3440
Cascade Impactor	BGI-30 High Volume Cascade Impactor 2 stages (No. 1 and 2)BGI Inc.Waltham,Ma.
Peristaltic pump silicone	Silichem 1/8" Bore, 1/4" O.D., New Brunswick
rubber tube	Scientific International Inc., New Brunswick, New Jersey.
Liquid Level Controller	Dyna-Sense Controller, Model 7188
Liquid Level Controller Probe	Dyna-Sense Sensing Probe Cat.No. 7186-12
Temperature Controller	Versa Therm Model 2158
Temperature Controller Probe	Versa Therm Liquid Immersion 8446
Immersion Cooler	Fabricated from Glass
Refrigerator	1.5 ft^3 Sears Cat. No. 3467370N, Sears Roebuck & Co.
Pump	Oscillating type, Model 7103-10 cap. 1/2 GPM at O'head, Cole Palmer Inst. Co., Chicago, Il.
T_1	4 circuit Egal BL 340 Timer, 6 hr.
T_2	Daton 2E026, Prog. Time Control (Variable On-off 4/hr to 1/day in 96 steps)
S	SPST Switch
S_1	SP3T Switch
S_2	SP2T Switch
S_3	SPST Switch
Magnetic Stirrer	Fabricated using 240 Kpm sychronour motor
Stirring Bar	3/8" Dia x 3/8"
14 Relays [K_1 - K_{15}]	Daton, 4 x 809, 115 V SPDT Relay

APPENDIX A

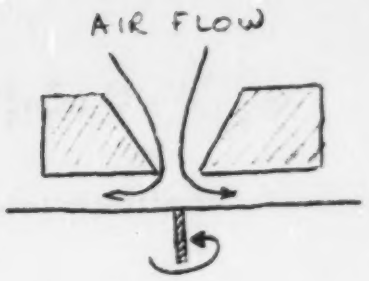
LIST OF COMPONENTS (CONTINUED)

Component	Description
9 Valves [V_1 - V_9]	Asco Solenoid Valve, Cat. No. 836015
Connecting Tubing	Teflon, 1 mm Dia.
4 Reservoirs	2 Gal and 1/2 Gal Plastic Carboy
Cabinet	Bud CR 1737

APPENDIX B

ESTIMATE OF ABSORPTION IN LEAP SAMPLER

The geometry of the LEAP sampler is schematically shown below.



We shall examine the absorption from the gas stream entering at the center and flowing outward to the edge of the dish. This portion of the inlet gas will exhibit maximum absorption. We will neglect any rotational effects due to the motion of the collecting plate. Considering an infinitesmal annual section at radius, r, from the center, we can write a material balance for the absorbent species in the gas, for example, nitrogen dioxide, as follows:

$$FC - F\left[C + \frac{dc}{dr}\,dr\right] - k\,2\pi r\,dr\,[C - C_i] = 0 \qquad \text{(C-1)}$$

where F = gas flow rate in cc/min

k = mass transfer coefficient in cm^2/min

C = concentration of absorbed species in moles/cc

C_i = equilibrium concentration above liquid

This reduces to:

$$F\,\frac{dc}{dr} = -\,k\,2\pi r\,[C - C_i] \qquad \text{(C-2)}$$

and can be integrated between any two radii as:

$$\int_{C_1}^{C_2} \frac{dc}{C-C_i} = -\frac{k2\pi}{F} \int_{r_1}^{r_2} r\,dr \qquad (C\text{-}3)$$

or

$$\ell n \frac{C_1-C_i}{C_2-C_i} = \frac{k\pi}{F}(r_2^2-r_1^2) \qquad (C\text{-}4)$$

The equilibrium concentration of nitrogen oxide is essentially zero so this simplifies to

$$\frac{C_2}{C_1} = e^{-\frac{k\pi}{F}(r_2^2-r_1^2)} \qquad (C\text{-}5)$$

In order to evaluate the expression on the right, we must know the value of the mass transfer coefficient. Being conservative, we assume the diffusion is mass transfer controlled (gas side). This is the fastest rate feasible, even if liquid-side chemical reaction is infinitely rapid.

Consider the case of flow over a flat plate. For gases (air), the Schmidt number (N_{sc}) is approximately unity, so that

$$N_{sh} \cong 0.6\ Re_r^{0.5} \qquad (C\text{-}6)$$

where N_{sh} = Sherwood number = $\frac{kr}{D}$

Re = Reynolds number = $\frac{V\rho r}{\mu}$

k = mass transfer coefficient

r = radius

D = diffusivity in cm/sec

ρ = gas density in gm/cc

μ = gas in viscosity

V = velocity in cm/sec

Using dimensions, characteristic of the sampler, at 500 l/min flow, the Reynolds number is

$$Re \cong 10^3$$

so that

$$\frac{kr}{D} = 6 \times (1000)^{0.5} \cong 19 \qquad \text{(C-7)}$$

For gas, the diffusivity is about 0.1 cm^2/sec, so that for a total travel distance (r) of 15 cm,

$$k \cong 0.12 \text{ cm/sec} \cong 7.2 \text{ cm/min}$$

Now, returning to Equation C-5, we find that the ratio of concentration from center to edge is

$$\frac{C_2}{C_1} = e^{-\frac{7.2 \times \pi}{F}(15^2 - 0^2)}$$

and, at

$$F = 500 \text{ l/min} = 5 \times 10^5 \text{ cc/min}$$

we find that

$$\frac{C_2}{C_1} \cong e^{-0.01} \cong 1$$

This calculation indicates that no significant absorption will occur during the passage of the gas through the sampler.

APPENDIX C

ATMOSPHERIC TEST DATA
BY TEST

This Appendix shows the test data by individual tests. The following notations were used:

B.F. = backup filter to the LEAP sampler
S_1 = first inspection stage
S_2 = second inspection stage
F_x = multiplying factor where analysis was performed on 1/2 or 1/4, etc. of filter area.

Test No. 1

Date: (8/21/74)-

	Sampling Rate, (m^3/min)	Sampling Time, (min)	Total Sampled Volume, (m^3)	Moles NO_3 Collected (μ moles)	F X	Total Moles NO_3 (μ moles)	Weight Nitrate Collected (μg)	Nitrate Concentration ($\mu g/m^3$)
Hi Vol A	1.67	1455	2430	58.0	9	522	32364	13.3
Hi Vol B	1.47	1455	2139	48.0	9	432	26784	12.5
Hi Vol C	1.75	1455	2546	64.0	9	576	35712	14.0
Av. Hi Vols.								13.3
B.F.	0.57	1455	829	4.1	4	16.4	1016.8	1.2
S_1	0.57	1455	829	2.05	2	4.1	254.2	0.31
S_2	0.57	1455	829	1.75	2	3.5	217.0	0.26
Cell	0.57	1455	829	87.0	1	87.0	5394.0	6.5

Test No. 2

Date: (8/22/74)

	Sampling Rate, (m^3/min)	Sampling Time, (min)	Total Sampled Volume, (m^3)	Moles NO_3 Collected (μ moles)	F X	Total Moles NO_3 (μ moles)	Weight Nitrate Collected (μg)	Nitrate Concentration ($\mu g/m^3$)
Hi Vol. A	1.27	1425	1810	37.2	4	148.8	9225.6	5.1
Hi Vol. B	1.41	1425	2009	40.0	4	160.0	9920.0	4.9
Hi Vol. C	1.39	1425	1980	39.2	4	156.8	9721.6	4.9
Av. Hi Vols.								4.9
B.F.	0.60	1425	855	1.7	4	6.8	421.6	0.50
S_1	0.60	1425	855	0.8	2	1.6	99.2	0.12
S_2	0.60	1425	855	2.1	2	4.2	260.4	0.30
Cell	0.60	1425	855	54.0	1	54.0	3348	3.9

Test No. 3

Date: (8/26/74)

	Sampling Rate, (m^3/min)	Sampling Time, (min)	Total Sampled Volume, (m^3)	Moles NO_3 Collected (μ moles)	F X	Total Moles NO_3 (μ moles)	Weight Nitrate Collected (μg)	Nitrate Concentration ($\mu g/m^3$)
Hi Vol. A	1.27	1300	1651	31.4	4	125.6	7787.2	4.7
Hi Vol. B	1.47	1300	1911	33.4	4	133.6	8283.2	4.3
Hi Vol. C	1.39	1300	1807	34.2	4	136.8	8481.6	4.7
Av. Hi Vol.								4.6
B.F.	0.6	1300	780	2.07	4	8.3	514.6	0.66
S_1	0.6	1300	780	0.56	2	1.1	68.2	0.09
S_2	0.6	1300	780	1.83	2	3.7	229.4	0.29
Cell	0.6	1300	780	41.4	1	41.4	2566.8	3.3

Test No. 4
Date:(8/29/74)

	Sampling Rate, (m^3/min)	Sampling Time, (min)	Total Sampled Volume, (m^3)	Moles NO_3 Collected (μ moles)	F X	Total Moles NO_3 (μ moles)	Weight Nitrate Collected (μg)	Nitrate Concentration ($\mu g/m^3$)
Hi Vol. A	1.42	1425	2023	35.6	4	142.4	8829	4.4
Hi Vol. B	1.61	1425	2294	41.6	4	166.4	10317	4.5
Hi Vol. C	1.47	1425	2095	43.6	4	174.4	10813	5.2
Av. Hi Vols.								4.7
B.F.	0.6	1425	855	2.3	4	9.31	577	0.68
S_1	0.6	1425	855	0.02	2	0.04	2.5	0.00
S_2	0.6	1425	855	0.55	2	1.10	68	0.08
Cell 1	0.6	105	63	2.7	1	2.7	167	2.65
2	"	"	"	3.3	"	3.3	205	3.25
3	"	"	"	2.04	"	2.04	126	2.01
4	"	"	"	2.04	"	2.04	126	"
5	"	"	"	2.04	"	2.04	126	"
6	"	"	"	4.5	"	4.5	279	4.23
7	"	"	"	5.1	"	5.1	316	5.02
Cell Av.								3.02

Test No. 5

Date: (9/3/74)

	Sampling Rate, (m^3/min)	Sampling Time, (min)	Total Sampled Volume, (m^3)	Moles NO_3 Collected (μ moles)	F X	Total Moles NO_3 (μ moles)	Weight Nitrate Collected (μg)	Nitrate Concentration ($\mu g/m^3$)
Hi Vol. A	1.29	1465	1890	12.6	4	50.4	3125	1.7
Hi Vol. B	1.63	1465	2388	13.0	4	52.0	3224	1.4
Hi Vol. C	1.44	1465	2110	16.6	4	66.4	4117	2.0
Av. Hi Vols.								1.6
B.F.	0.6	1465	879	2.0	4	8.0	496	0.56
S_1	0.6	1465	879	0.0	2	0.0	0.0	0.0
S_2	0.6	1465	879	0.14	2	0.3	18.6	0.02
Cell 1	0.6	105	63	3.9	1	3.9	242	3.8
2	"	"	"	2.6	"	2.6	161	2.6
3	"	"	"	2.4	"	2.4	149	2.4
4	"	"	"	2.3	"	2.3	143	2.2
5	"	"	"	2.4	"	2.4	149	2.4
6	"	"	"	2.4	"	2.4	149	2.4
7	"	"	"	1.3	"	1.3	81	1.3
8	"	"	"	1.3	"	1.3	81	1.3
9	"	75	45	0.7	"	0.7	43	1.0
Cell Av.								2.1

Test No. 6

Date: (9/5/74)

	Sampling Rate, (m^3/min)	Sampling Time, (min)	Total Sampled Volume, (m^3)	Moles NO_3 Collected (μ moles)	F X	Total Moles NO_3 (μ moles)	Weight Nitrate Collected (μg)	Nitrate Concentration ($\mu g/m^3$)
Hi Vol. A	1.39	1430	1988	24.3	4	97.2	6026	3.0
Hi Vol. B	1.64	1430	2345	25.5	4	102	6324	2.7
Hi Vol. C	1.44	1430	2059	33.1	4	132.4	8209	4.0
Av. Hi Vols								3.2
B. F.	0.6	1430	858	1.7	4	6.8	422	0.5
S_1	0.6	1430	858	0.25	2	0.5	31	0.03
S_2	0.6	1430	858	0.65	2	1.3	81	0.09
Cell 1	0.6	105	63	1.38	1	1.38	86	1.4
2	"	"	"	1.38	"	1.38	86	1.4
3	"	"	"	1.44	"	1.44	89	1.4
4	"	"	"	1.08	"	1.08	67	1.1
5	"	"	"	1.08	"	1.08	67	1.1
6	"	"	"	1.44	"	1.44	89	1.4
7	"	"	"	1.44	"	1.44	89	1.4
8	"	"	"	1.56	"	1.56	97	1.5
9	"	"	"	1.44	"	1.44	89	1.4
10	"	"	"	1.56	"	1.56	97	1.5
Cell Av.								1.4

Test No. 7

Date: (9/9/74)

	Sampling Rate, (m^3/min)	Sampling Time, (min)	Total Sampled Volume, (m^3)	Moles NO_3 Collected (μ moles)	F X	Total Moles NO_3 (μ moles)	Weight Nitrate Collected (μg)	Nitrate Concentration (μg/m^3)
Hi Vol. A	1.39	1410	1960	56.2	4	224.8	13938	7.1
Hi Vol. B	1.58	1410	2228	60.2	4	240.8	14929	6.7
Hi Vol. C	1.44	1410	2030	62.2	4	248.8	15426	7.6
Av. Hi Vols.								7.1
B.F.	0.6	1410	846	2.3	4	9.1	565	0.67
S_1	0.6	1410	846	0.42	2	0.8	52	0.06
S_2	0.6	1410	846	0.77	2	1.5	95	0.11
Cell 1	0.6	105	63	2.0	1	2.0	124	2.0
2	"	"	"	1.3	"	1.3	81	1.3
3	"	"	"	1.3	"	1.3	81	1.3
4	"	"	"	1.5	"	1.5	93	1.5
5	"	"	"	1.2	"	1.2	74	1.2
6	"	"	"	1.3	"	1.3	81	1.3
7	"	"	"	1.5	"	1.5	93	1.5
8	"	"	"	1.9	"	1.9	118	1.8
9	"	"	"	2.5	"	2.5	155	2.5
10	"	"	"	2.0	"	2.0	124	2.0
11	"	"	"	1.8	"	1.8	112	1.8
12	"	"	"	2.4	"	2.4	149	2.4
Cell Av.								1.7

Test No. 8

Date: (9/10/74)

	Sampling Rate, (m^3/min)	Sampling Time, (min)	Total Sampled Volume, (m^3)	Moles NO_3 Collected (μ moles)	F X	Total Moles NO_3 (μ moles)	Weight Nitrate Collected (μg)	Nitrate Concentration ($\mu g/m^3$)
Hi Vol. A	1.30	1595	2073	297	4	1188	73656	35.5
Hi Vol. B	1.50	1595	2393	237	4	948	58776	24.6
Hi Vol. C	1.35	1595	2153	397	4	1588	98456	45.7
Av. Hi Vols.								35.0
B.F.	0.57	1595	909	5.6	2	11	696	0.76
S_1	0.57	1595	909	2.0	2	4	248	0.27
S_2	0.57	1595	909	2.6	2	5	310	0.34
Cell 1	0.6	105	63	3.6	1	3.6	223	3.5
2	0.6	"	63	2.5	"	2.5	155	2.5
3	0.6	"	63	2.4	"	2.4	149	2.4
4	0.6	"	63	2.4	"	2.4	149	2.4
5	0.5	"	52	2.9	"	2.9	180	3.4
6	0.5	"	52	4.0	"	4.0	248	4.7
7	0.5	"	52	4.6	"	4.6	285	5.4
8	0.5	"	52	3.6	"	3.6	223	4.2
9	0.6	"	63	2.9	"	2.9	180	2.8
10	0.6	"	63	4.1	"	4.1	254	4.0
11	0.6	"	63	4.3	"	4.3	267	4.2
12	0.6	"	63	3.1	"	3.1	192	3.0
Cell Av.								3.5

Test No. 9

Date: (9/12/74)

	Sampling Rate, (m^3/min)	Sampling Time, (min)	Total Sampled Volume, (m^3)	Moles NO_3 Collected (μ moles)	F X	Total Moles NO_3 (μ moles)	Weight Nitrate Collected (μg)	Nitrate Concentration ($\mu g/m^3$)
Hi Vol. A	1.2	1440	1728	34.0	4	136.0	8432	4.9
Hi Vol. B	1.5	1440	2160	34.0	4	136.0	8432	3.9
Hi Vol. C	1.3	1440	1872	35.6	4	142.4	8829	4.7
Av. Hi Vols.								4.5
B.F.	0.5	1440	720	2.7	4	10.9	677	0.93
S_1	0.5	1440	720	0.8	2	1.6	99	0.14
S_2	0.5	1440	720	1.6	2	3.2	201	0.28
Cell 1	0.5	1440	720	39	1	39	2418	3.3
2								
3								

Test No. 10

Date: (9/16/74)

	Sampling Rate, (m^3/min)	Sampling Time, (min)	Total Sampled Volume, (m^3)	Moles NO_3 Collected (μ moles)	F X	Total Moles NO_3 (μ moles)	Weight Nitrate Collected (μg)	Nitrate Concentration ($\mu g/m^3$)
Hi Vol. A	1.39	1440	2002	13.8	4	55	3422	1.7
Hi Vol. B	1.58	1440	2275	15.8	4	63	3918	1.7
Hi Vol. C	1.44	1440	2074	17.8	4	71	4414	2.1
Av. Hi Vols.								1.8
B.F.	none used							
S_1	0.6	1440	864	~ 0	2	~0	~0	~0
S_2	0.6	1440	864	0.2	2	0.4	26	0.03
Cell	0.6	1440	864	25.8	1	26	1600	1.8